FOR SUBMISSION TO *PHYSICA D.* Today's version February 7, 2008

Clumps and patches in self-aggregation of finite size particles

Darryl D. Holm[1,2] and Vakhtang Putkaradze[3]

[1]Theoretical Division
Los Alamos National Laboratory, Los Alamos, NM 87545, USA
email: dholm@lanl.gov
and
[2]Mathematics Department
Imperial College London, SW7 2AZ, UK
email: d.holm@imperial.ac.uk

[3]Department of Mathematics and Statistics
University of New Mexico, Albuquerque, NM 87131-1141
email: putkarad@math.unm.edu

February 7, 2008

Abstract

New model equations are derived for dynamics of self-aggregation of finite-size particles. Differences from standard Debye-Hückel [1] and Keller-Segel [2] models are: a) the mobility μ of particles depends on the locally-averaged particle density and b) linear diffusion acts on that locally-averaged particle density. The cases both with and without diffusion are considered here. Surprisingly, these simple modifications of standard models allow progress in the analytical description of evolution as well as the complete analysis of stationary states. When

μ remains positive, the evolution of collapsed states in our model reduces exactly to finite-dimensional dynamics of interacting particle clumps. Simulations show these collapsed (clumped) states emerging from smooth initial conditions, even in one spatial dimension. If μ vanishes for some averaged density, the evolution leads to spontaneous formation of *jammed patches* (weak solution with density having compact support). Simulations confirm that a combination of these patches forms the final state for the system.
Keywords: gradient flows, blow-up, chemotaxis, parabolic-elliptic system, singular solutions

Contents

1 Historical perspective of continuum models of self-aggregation

Many fields of physics, chemistry and biology deal with the problem of describing the evolution of the macroscopic density of a large number of particles, which self-consistently attract each other over distances large compared to their mean separation. A related paradigm arises in biosciences, particularly in chemotaxis: the study of the influence of chemical substances in the environment on the motion of mobile species which secrete these substances. One of the most famous among such models is the Keller-Segel elliptic-parabolic system of partial differential equations [2], which was introduced to explore the effects of nonlinear cross diffusion in the formation of aggregates and patterns by chemotaxis in the aggregation of the slime mold *Dictyostelium discoidium*. The Keller-Segel model consists of two strongly coupled reaction-diffusion equations,

$$\rho_t + \mathrm{div}\mathbf{J} = 0 \qquad \mathbf{J} = \rho\mu(\Phi)\nabla\Phi - D\nabla\rho \qquad \epsilon\Phi_t + L\Phi = \gamma\rho\,, \qquad (1)$$

expressing the coupled evolution of concentration of organisms (density) ρ and concentration of chemotactic agent (potential) Φ. These challenging nonlinear equations were posed for chemotaxis as an initial value problem with Neumann boundary conditions initial data. The constants $\gamma, D, \epsilon > 0$ are assumed to be positive and $\mathbf{J}$ is the flux of organisms (particles). The linear operator L is taken to be positive and symmetric. For example, one may choose it to be the Laplacian $L = -\Delta$ or the Helmholtz operator, $L = 1 - \alpha^2\Delta$. For the moment, the functional dependence of the mobility μ will be left unspecified.[1] The "simplified" Keller-Segel model is obtained by setting $\epsilon = 0$ in (1). Because of its fascinating mathematical properties – such as finite-time concentration of the density ρ into Dirac delta-function singularities, starting from smooth initial conditions – and its relevance to chemotaxis, the Keller-Segel system has attracted sustained interest in mathematical biology. To avoid excessive citation here, we shall only refer to the review article [3] where over 150 references on the role of (1) in the chemotaxis problem may be found.

[1] One recovers the precise expression of Keller and Segel [2] by rewriting the mobility term as $\mu(\Phi)\nabla\Phi = \nabla\chi(\Phi)$, where $\chi(\Phi)$ is the "sensitivity function." The development below introduces a different functional dependence in the mobility μ.

The applications of equations in the form of system (1) in physics and chemistry may be traced back into the 19th century. The history of these equations is a story of recurrent rediscovery, each time as a leading order description of singularity formation, occurring as the tendency to diffuse is eventually overwhelmed by long-range forces of attraction. Quite likely, their story has not finished yet and these equations will be needed again for the insights they provide into nonlinear multiscale dynamics in the competition between coalescence and diffusion.

Three main modeling steps figure in the derivation of (1) and similar equations. First, the flux $\mathbf{J}$ must be modeled in terms of the local particle density, its spatial gradient and the gradient of the potential. Second, an equation must be formulated for determining the potential Φ from the local density ρ. Third, conservation of mass, charge, or particle number must be introduced as the evolution equation for density.

Historically, it seems that Debye and Hückel in 1923 were the first to put all three of these modeling steps together. They derived the evolutionary system (1) in their article [1] on the theory of electrolytes. In particular, the simplified model with $\epsilon = 0$ in (1) may be found as equations (2) and $(2')$ in Debye and Hückel [1]. Consequently, the simplified evolutionary system (1) with $\epsilon = 0$ may also be called the Debye-Hückel equations.

The Debye-Hückel equations (1) with $\epsilon = 0$ also appeared very early in astrophysics as the Poisson-Smoluchowski system, a particular Fokker-Planck equation describing a self-attracting reinforced random walk of particles (with mass, but without inertia) diffusing by local collisions and drifting against friction under their mutual long-range attraction. As is well known, gravitational force leads to collapse in this case, when mutual attraction finally prevails over diffusion and friction. See Chandrasekhar (1939) [4] for an exhaustive historical review from the viewpoint of stellar formation.

Interest in the Debye-Hückel system was recently revived, when the "Nernst-Planck" (NP) equations in the same form as (1) re-emerged in the biophysics community, for example, in the study of ion transport in biological channels. In this case, the flux $\mathbf{J}$ is called the Nernst-Planck (NP) particle flux for the ion current density $\mathbf{J}$ depending linearly on the gradients $(\nabla\rho, \nabla\Phi)$ and L is the Laplace operator. See Barcilon et al. (1992) [5] and Syganow and von Kitzing (1999) [7] for recent reviews of ion transport in biological media. The same elliptic-parabolic system had also surfaced earlier as the "drift-diffusion" equations in the semiconductor device design literature, Selberherr (1984) [8]. Similar elliptic-parabolic equations (with hyper-diffusion, instead

of diffusion) also arose recently as a leading order description of molecular beam epitaxy [9]. A variant of the system (1) re-appeared even more recently as a model of self-assembly of particles at nano-scales [11].

2 Derivation of aggregation equation for finite-size particles and variable mobility

In this paper, we modify the class of Debye-Hückel equations (1) with $\epsilon = 0$, as a model of the aggregation of interacting particles of finite size. This problem is motivated by recent experiments using self-assembly of nano-particles in the construction of nano-scale devices [12]-[20]. A colloidal solution of 50nm-size particles is deposited on a grooved substrate; evaporation and receding contact line drags the particles into the channels. It has been shown [11] that the most important phenomenon effecting the distribution of particles in the channels is the capillary interaction between the particles at last stage of water evaporation, when all water and particles are confined to the channels. Examples of particle self-assembly in nano-channels is shown inFig. 1. Fundamental principles underlying the mathematics of self-assembly at the nano-scales are non-local particle interaction and nonlinear motion due to variations of mobility at these scales.

Let us start by deriving the effective interaction potential between nano-particles. This will reveal the length scales involved in the problem and characterize the type of interaction between the particles. Due to the effects of surface tension, the air/water interface is deformed near a particle. On the other hand, water is attracted to the substrate surface by van der Waals forces. Denote the thickness of the undisturbed water layer by H_0 and let h be the elevation from this equilibrium level. If we call the potential of van der Waals interaction $U_{vdW}(H)$, then for small deviations from the equilibrium surface the balance of surface tension and van der Waals force gives

$$\gamma \Delta h = F_0 h, \qquad F_0 = -\frac{\partial U_{vdW}}{\partial H}(H = H_0) \tag{2}$$

A typical expression for van der Waals potential includes three terms [21]

$$U_{vdW}(H) = \frac{A}{H^3} - \frac{B}{H^\kappa} - Ce^{-H/l_0} \tag{3}$$

with constants A, B, C, with $\kappa > 3$ and l_0 being the interaction length. A numerical estimate for these values from [21] shows that for $H \sim 50$ nm,

the first term on the right-hand side of (3) is larger than the second and third terms by factors 10^9 and 10^{18}, respectively. Here, A is called *Hamaker constant*, which assumes a certain value for a given pair of materials.[2] Then, (2) can be re-written in terms of *capillary length* l_c as

$$l_c^2 \Delta h - h = 0 \qquad l_c = H_0^2 \sqrt{\frac{\sigma}{3A}} \tag{4}$$

where we have applied the term *capillary length* even though the stabilizing potential is due to van der Waals forces and not gravity. Numerical values for Hamaker constant for water on silicon is about $30zJ = 30 \cdot 10^{-21} J$, surface tension of water/air interface is $0.07 N/m$. Consequently, for $H_0 = 50$nm, equation (4) yields capillary length $l_c \simeq 300$nm, or several times the particle diameter.

It is now clear that in spite of very different physics and length scales, the phenomenon of self-attraction of particles at nano-scales bears not just qualitantive, but also quantitative resemblance to the well-known *Cheerios effect*: self-attraction of floating bodies due to surface tension. For floating cheerios, the typical length of interaction is the usual capillary length (several mm), which is also of the order of particle size. It has been shown [22, 23] that two particles separated by a distance l have interaction potential proportional to $\exp(-l/l_c)$ in one dimension, and $K_0(l/l_c)$ in two dimensions ($K_0(x)$ being the modified Bessel function of the first kind). The force between the particles is then proportional to $K_1(l/l_c)$, and this result holds for both floating and partially submerged particles. Mathematically, these interaction potentials arise from inversion of Helmholtz operator in (4).

These physical considerations show that interaction potentials proportional to the Green's function for the Helmholtz operator plays a fundamental role in particle self-assembly across surprisingly many orders of magnitude. Thus, we shall consistently use this interaction potential in all our numerical simulations. Nevertheless, we shall keep our framework general enough that our method of modeling nonlocal interactions among different particles may be extended to the other physical problems of interest described in the previous section. Our method takes into account the change of mobility due to the finite size of particles and the nonlocal interaction among the particles. The local density (concentration) of particles is denoted by ρ. Suppose the

[2]Usually, the numerical vallue of A is given in *zJoules*, with z being used for *zepto*$= 10^{-21}$.

particles interact pairwise via the potential $-G(|\mathbf{r}|)$. The total potential at a point $\mathbf{r}$ is

$$\Phi(\mathbf{r}) = -\int \rho(\mathbf{r}')G(|\mathbf{r}-\mathbf{r}'|)\mathrm{d}\mathbf{r}' = G * \rho \tag{5}$$

where $*$ denotes convolution. (The minus sign is chosen so $G > 0$ for attracting particles.) The velocity of the particle is assumed to be proportional to the gradient of the potential times the mobility of a particle, μ. The mobility can be computed explicitly for a single particle moving in an infinite fluid. However, when several particles are present, especially in highly dense states, the mobility may be hampered by the particle interactions. These considerations are confirmed, for example, by the observation that the viscosity of a dense suspension of hard spheres in water diverges, when the density of spheres tends to its maximum value. Many authors have tried to incorporate the dependence of mobility on local density by putting $\mu = \mu(\rho)$ [24]. It is common to assume that the mobility is a function of density, which tends to zero when the density tends to some maximum value, assumed to be $\rho_{\max} = 1$, *i.e.*, $\mu(\rho_{\max}) = 0$. Vanishing mobility leads to the appearance of weak solutions in the equations, to singularities and, in general, to massive complications and difficulties in both theoretical analysis and computational simulations of the equations. In contrast, the Keller-Segel model specifies $\mu(\Phi)$, so the mobility is taken in that case as a function of the concentration of chemotactic agent (potential) Φ.

The goal of this paper is to suggest and investigate the implications of the idea that the mobility μ should depend on the *averaged* density $\overline{\rho}$, rather than either the potential, or the exact value of the density at a point. This assumption makes sense from the viewpoints of both physics and mathematics. From the physical point of view, the mobility of a finite-size particle must depend on the configuration of particles in its vicinity. While attempts have been made to approximate this dependence by using derivatives of the local density, it is much more natural, in our opinion, to assume that the local mobility depends on an integral quantity $\overline{\rho}$ which is computed from the density as $\overline{\rho} = H * \rho$. Here $H(\mathbf{r})$ is some *filter* function having, in general, short range compared to the potential G. Several filter functions are possible, with examples being $H(\mathbf{r}) = \delta(\mathbf{r})$ (δ-function), $H(\mathbf{r}) = \exp(-|\mathbf{r}|/l)/(2l)$ (exponential, or inverse-Helmholtz in 1D) or, in d dimensions, $H(\mathbf{r}) = \theta(|\mathbf{r}|-l)/(2l)^d$. The last is the top-hat function, whose value is unity when $|\mathbf{r}|$ is between $-l$ and l, and vanishes, elsewhere. The normalizing factor of $(2l)^d$ (d being the dimension of space) is introduced so that $\int_{-\infty}^{+\infty} H(\mathbf{r})\mathrm{d}\,\mathbf{r} = 1$. Alternatively,

one may assume a filter function $H(\mathbf{r})$ with zero average: $\int_{-\infty}^{+\infty} H(\mathbf{r})\mathrm{d}\,\mathbf{r} = 0$. The latter assumption may be useful in crystal growth models, where the mobility does not depend on the absolute level of the material. Rather, in such models the mobility depends on the relative positioning of particles. The mathematical analysis and the reduction property derived in this paper hold, regardless of the shape of the filter function H and the potential G is, so long as they are both *nice* (*e.g.*, piecewise smooth) functions.

Aim of the paper The object of this paper is the analysis of the following continuity equation for density evolution,

$$\underbrace{\frac{\partial \rho}{\partial t} = -\operatorname{div} \mathbf{J}}_{\text{Continuity equation}} \qquad \text{with} \qquad \underbrace{\mathbf{J} = -D\nabla\overline{\rho} - \mu(\overline{\rho})\rho\nabla\Phi}_{\text{Particle flux}} . \tag{6}$$

Here D is a constant diffusivity, while $\overline{\rho}$ and Φ are defined by two convolutions involving, respectively, the filter function H and the potential G,

$$\overline{\rho} = H * \rho \quad \text{and} \quad \Phi = G * \rho\,. \tag{7}$$

While this equation preserves the sign of ρ, we shall see that it allows the formation of δ-function singularities even when $D > 0$ and in the case of one spatial dimension.

Alternatively, system (6,7) with $D = 0$ can be represented geometrically as

$$\frac{d}{dt}(\rho\,\mathrm{dVol}) = 0 \quad \text{along} \quad \frac{d\mathbf{x}}{dt} = \mathbf{J}(\rho)\,,$$

where the vector field corresponding to the current $\mathbf{J}(\rho)$ is defined in terms of the pointwise density $\rho \geq 0$ and two prescribed functionals of ρ: an energy $E(\rho)$ and a mobility $\mu(\overline{\rho}) \geq 0$, as

$$\mathbf{J}(\rho) = -\rho\mu(\overline{\rho})\nabla\frac{\delta E}{\delta \rho}\,.$$

Here $\overline{\rho} = H * \rho \geq 0$ is an average density. As a result,

$$\frac{d}{dt}E(\rho) = -\int \frac{1}{\rho\mu(\overline{\rho})}\,|\mathbf{J}(\rho)|^2\mathrm{dVol} \leq 0\,.$$

Thus, the flow $d\mathbf{x}/dt = \mathbf{J}$ causes the energy functional $E(\rho)$ to decrease toward its minimum value and the flow is Lyapunov stable, provided the energy

functional $E(\rho)$ is sign definite and $\mu(\overline{\rho})$ is isolated from 0. We may regard $\mathbf{J}$ as a vector field defining an infinitesimal action of the diffeomorphisms on the space of positive maps ρ acting on a manifold $\mathcal{M}$. Remarkably, this action produces singularities in which the pointwise density concentrates in finite time on subspaces embedded in the manifold $\mathcal{M}$.

Subcases The generality and predictive power of the model (6,7) can be demonstrated by enumerating a few of its subcases, as follows. When $H(\mathbf{r}) = \delta(\mathbf{r})$ and $G(x) = e^{-|\mathbf{r}|/l}$ the system reduces to the generalized chemotaxis equation [24]. For the choice $G = \delta'(\mathbf{r})$, $H = \delta'(\mathbf{r})$ one obtains a modification of the inviscid Villain model for MBE evolution [9] (with extra factor of ρ in the flux). If the range of G (denoted by l) is sufficiently small, we can approximate (at least formally) the integral operator in $\Phi = G * \rho$ as a differential operator acting on the density ρ, namely,

$$\Phi = \rho + l\nabla \cdot (l\nabla\rho)\,.$$

As was demonstrated in [11], equation (6) then becomes a generalization of the viscous Cahn-Hilliard equation, describing aggregation of domains of different alloys. In the case that μ is a constant, $H(x-y) = \delta(x-y)$, and G is the Poisson kernel, then equation (6) becomes the drift limit of the Poisson-Smoluchowski equation for the interaction of gravitationally attracting particles under Brownian motion [4].

All the particular cases described above require a singular choice of the functions G and H. However, the generalized functions required in these cases may be approximated with arbitrary accuracy by using sequences of nice (for example, piecewise smooth) functions. We shall concentrate on cases where the functions H and G remain nice, and derive the results in this more general, more regular, setting. Thus, regularization in this endeavor introduces additional generality, which enables analytical progress and makes numerical solution of the equations easier.

3 Evolution of density as mass conserving gradient flow: the nonlocal Darcy's law and energetic considerations

Let us have another look at our motivation of equations (6,7), this time making a connection with gradient flows and thermodynamics. We will show that there is a naturally defined free energy which remains finite, even when the solutions cease to be smooth and are replaced by a set of delta-functions. We show that the energy remains finite for all choices of $\mu(\overline{\rho})$. In contrast, the traditional approach considering the dependence of mobility on the unsmoothed density $\mu(\rho)$ would fail by allowing the energy to become infinite. This additional energetic argument reinforces the choice of the regularized model in (6,7). The calculation will be performed in arbitrary spatial dimensions.

For the energy to be well-defined, we require that the function G describing interaction between two particles is everywhere positive, so the interaction is always attractive. In one dimension, we also require that the kernel function G is symmetric and in n dimensions that the interaction is central. This assumption is physically viable for all the historical cases described in the introduction. Our derivation for the free energy will remain valid for an *arbitrary* filter function H.

We start with equation (6) for mass conservation, in the case when the mobility $\mu(\overline{\rho})$ in the particle flux $\mathbf{J}$ is not constant. We shall derive a variant of equation (6) as a gradient flow in the sense that,

$$\frac{\partial \rho}{\partial t} = -\operatorname{grad} E|_{\rho}\,, \quad \text{or} \quad \Big\langle \frac{\partial \rho}{\partial t}\,,\, \phi \Big\rangle = -\Big\langle \frac{\delta E}{\delta \rho}\,,\, \phi \Big\rangle\,,$$

where $\langle f\,,\,\phi\rangle = \int f\phi\, d^n x$ is the L^2 pairing, for a suitable test function ϕ and where E is the following energy,

$$E[\rho] = D\int \rho(\log\rho - 1)\mathrm{d}x + \frac{1}{2}\int \rho\,\Phi\,\mathrm{d}x \quad \text{with} \quad \Phi = G * \rho\,. \tag{8}$$

The first term in this expression for the energy $E[\rho]$ decreases monotonically in time for linear diffusion. The second term defines the H^{-1} norm for the choice $G(x) = \exp(-|x|/\alpha)$. It may be regarded as a generalization of this norm for an arbitrary (but positive and symmetric) function G. Such

negative Sobolev norms remain finite, even when the solution for the density ρ concentrates into a set of delta functions.

The variation $\delta E/\delta\rho$ of the free energy $E[\rho]$ in equation (8) is

$$\delta E[\rho] = \int (D\log\rho + \Phi)\,\delta\rho\, d^{\,n}x\,,$$

where we understand $\delta\rho$ as arising from the flow of a diffeomorphism, as for example in [25]. Namely, we specify

$$\delta\rho = -\mathrm{div}\Big(\rho\mu(\overline{\rho})\nabla\Psi\Big)\,,$$

for an arbitrary variation of ρ determined by the function Ψ, which is assumed to be smooth.[3] The corresponding variational derivative is given by, cf. [26]

$$\begin{aligned}\delta E[\rho] &= \Big\langle \frac{\delta E}{\delta\rho}\,,\,\Psi\Big\rangle = -\int (D\log\rho+\Phi)\,\mathrm{div}(\rho\mu(\overline{\rho})\nabla\Psi) d^{\,n}x \\ &= -\int \Psi\,\mathrm{div}\Big(\mu(\overline{\rho})(D\nabla\rho+\rho\nabla\Phi)\Big)\,d^{\,n}x\,. \end{aligned} \tag{9}$$

Consequently, the free energy $E[\rho]$ in equation (8) produces the following gradient flow:

$$\Big\langle \frac{\partial\rho}{\partial t}\,,\,\Psi\Big\rangle = -\Big\langle \frac{\delta E}{\delta\rho}\,,\,\Psi\Big\rangle = \Big\langle \mathrm{div}\Big(\mu(\overline{\rho})(\mathrm{D}\nabla\rho+\rho\nabla\Phi)\Big)\,,\,\Psi\Big\rangle\,.$$

The resulting variant of equation (6) is

$$\underbrace{\frac{\partial\rho}{\partial t} = -\,\mathrm{div}\,\mathbf{J}}_{\text{Continuity eqn}} \quad \text{with} \quad \underbrace{\mathbf{J} = -\,\mu(\overline{\rho})(D\nabla\rho+\rho\nabla\Phi)\Big)}_{\text{Modified particle flux}}\,, \tag{10}$$

in which the linear diffusivity of density ρ is modified by the nonlocal mobility $\mu(\overline{\rho})$.

[3]This specification of the density variation formally requires the solution to remain differentiable and the product $\rho\mu(\overline{\rho})$ not to vanish. In principle, these conditions would be violated by the formation of weak solutions, in which the density concentrates into delta-functions. However, we will verify *a posteriori* that the gradient flow properties of the smooth solutions discussed in this section are also preserved for the weak solutions.

Energetics The free energy $E[\rho]$ in (8) decreases monotonically in time under the evolution equation (10). A direct calculation yields,

$$\frac{dE[\rho]}{dt} = -\int (D\log\rho + \Phi)\,\mathrm{div}\,\mathbf{J}\,d^n x = -\int \frac{1}{\rho\mu_(\overline{\rho})}\,|\mathbf{J}|^2\,d^n x\,. \qquad (11)$$

According to this equation, provided $\rho\mu_(\overline{\rho}) > 0$, the rate of decay of free energy $E[\rho]$ given in (8) defines a Riemannian metric in the particle flux, cf. [26]. We shall see that when $D = 0$, the resulting conservative motion of finite-size particles drifting along the gradient of Φ leads to a type of 'clumping' of the density ρ into a set of delta functions. One may check that this monotonic decrease of energy persists for more general functions, including weak solutions supported on δ-functions, as discussed below.

4 Non-vanishing mobility: weak solutions (*clumpons*) and their role in long-term dynamics in 1D

Everywhere in this paper, we shall assume that the potential is purely attractive, so $G(x) > 0$ for all x. This assumption is used for two main reasons. First, it suits the physics of the motivating problem, namely, mutual attraction of nano-particles [10]. Second, restricting to purely attractive interactions allows one to separate all equations of the type (6,7) into two different classes. The physical property separating the two classes is whether the mobility $\mu(\overline{\rho})$ is strictly isolated from zero, i.e., $\mu(\overline{\rho}) \geq \mu_0 > 0$ or one may allow $\mu(\overline{\rho}_0) = 0$ for some $\overline{\rho} = \overline{\rho}_0$. In the first case, there is nothing to resist the mutual attraction of the particles and the final state of the system is a single δ-function no matter what the form of the mobility dependence, as long as mobility is strictly isolated from zero. In the second case, vanishing of the mobility at some maximum density blocks the motion when the densities become too large and prevents total collapse. Instead of collapse, this produces isolated *patches* of solutions of constant density. It is interesting that also in this second case, the stationary solutions remain *exactly the same* regardless of the dependence of μ on $\overline{\rho}$, and we can describe these stationary solutions analytically. Moreover, we shall demonstrate that these solutions are stable and any initial condition separates into a set of isolated stationary patches of this type.

This section is devoted to analytical description of dynamics in the case when $\mu(\overline{\rho})$ being strictly isolated from zero. In simulations, we have assumed $\mu(\overline{\rho}) = 1$ for simplicity, but all our results will remain valid for arbitrary dependence of μ on $\overline{\rho}$, as long as μ always remains positive.

4.1 Formal weak solution anzatz

This section considers motion under equations (6,7) in one spatial dimension for the case of vanishing linear diffusivity, $D = 0$. Substituting the following singular solution ansatz

$$\rho(x,t) \;=\; \sum_{i=1}^{N} w_i(t)\delta(x - q_i(t))\,, \quad \overline{\rho}(x,t) = \sum_{j=1}^{N} w_j(t)H(x - q_j(t))\,, \tag{12}$$

into the one-dimensional version of equation (6) with $D = 0$ and integrating the result against a smooth test function ϕ yields

$$\begin{aligned}\int \phi\Big[\rho_t - \Big(\rho\,\mu(\overline{\rho})(G * \rho)_x\Big)_x\Big]dx &= \int \phi(x) \sum_{i=1}^{N} \dot{w}_i\,\delta(x - q_i)dx \\ &+ \int \phi\,'(x) \sum_{i=1}^{N} w_i\Big(\dot{q}_i + \sum_{j=1}^{N} w_j(t)\mu(\overline{\rho})G\,'(x - q_j)\Big)\delta(x - q_i)\,dx\end{aligned}$$

Hence, one obtains a closed set of equations for the parameters $w_i(t)$ and $q_i(t)$, $i = 1, 2, \ldots, N$, of the solution ansatz (12), in the form

$$\dot{w}_i(t) = 0\,, \quad \dot{q}_i(t) = -\sum_{j=1}^{N} w_j\mu(\overline{\rho})G\,'(q_i - q_j) \tag{13}$$

where

$$\overline{\rho} = \sum_{m=1}^{N} w_m H(q_m(t)) \tag{14}$$

Thus, the density weights $w_i(t) = w_i(0) = w_i$ are preserved, and the positions $q_i(t)$ follow the characteristics of the velocity $\mathbf{u} = -\mu(\overline{\rho})\nabla G * \rho$ along the Lagrangian trajectories at $x = q_i(t)$. This result holds in any number of dimensions, modulo changes to allow singular solutions supported along moving curves in 2D and moving surfaces in 3D. Fig. 2, demonstrates that the solutions (13) do indeed appear spontaneously in a numerical simulation

of equation (6) with $D = 0.02$. Hence, they are ubiquitous and dominate its dynamics. The simulation started with a smooth (Gaussian) initial condition for density ρ. Almost immediately, one observes the formation of several singular *clumpons*, which evolve to collapse eventually into a single clumpon. Observe that the mass of each individual clumpon remains almost exactly constant in the simulations, as required by equation (13). Also note that the masses of two individual clumpons add when they collide and "clump" together. Eventually, all the mass becomes concentrated into a single clumpon, whose mass (amplitude) is *exactly* the total mass of the initial condition.

4.2 Energy decay close to the final state and estimates for collapse time

Normally, systems approaching an equilibrium state tend to evolve more slowly as they approach the equilibrium. If the rate of approach diminishes linearly with the distance from equilibrium (in some sense), for example, one obtains an exponential decay towards the equilibrium. Alternatively, for finite-time singularities, the rate tends to diverge to infinity in a power-law fashion. In contrast to these familiar examples, the system (6,7) approaches the singularity at a *constant* rate. That is, the rate of approach to singularity never diverges. Consequently, one may predict the formation of singularities and even predict their evolution after they have formed.

This surprising result may be demonstrated by deriving an alternative form of energy dissipation. Direct substitution of a single δ-function for density into (11) is mathematically ambiguous, as it would lead to improper operations with δ-functions. Instead, let us notice that the evolution of the energy E describing the gradient flow of (6,7) can be expressed as follows

$$\frac{dE}{dt} = -\int G(x-x')\rho(x')\frac{\partial \rho(x)}{\partial t}\mathrm{d}x\mathrm{d}x' =$$

$$+\int \Phi \mathrm{div}\left(\rho\mu(\overline{\rho})\mathrm{grad}\Phi\right) = -\int \rho\mu(\overline{\rho})(\nabla\Phi)^2 \qquad (15)$$

Note the difference between this formula and (11). Formally, (15) is the same as (11), but we can substitute the delta-function ansatz for weak solutions directly into (15).

Numerical simulations, energetic considerations and physical intuition suggest that the final state of the system with strictly positive mobility $\mu(\rho) \geq \mu_0 > 0$ should be a single clumpon. One may ask how the time

necessary to collapse to this final state varies with the initial conditions. An exact analytical answer to this question seems out of reach and we shall provide a numerical simulation for various initial conditions. However, a surprisingly simple and accurate analytical estimate can be made here. To start, let us compute the rate of energy dissipated by a single clumpon, which is the final state of our system. We assume $\rho = M\delta(x)$, where M is the total mass. Assuming that $H(x)$ is regular, $H * \rho(x) = MH(x)$. Let us also assume for simplicity that $G(x) = G_0 \exp(-|x|/\alpha)$. Direct computation gives

$$\frac{dE}{dt}[\rho = \text{clumpon}] = -M\mu\left(MH(0)\right)\left(\nabla\Phi(0)\right)^2 = -\frac{M^3}{\alpha^2}\mu\left(MH(0)\right)G_0^2 \quad (16)$$

We may now estimate how long it will take for an arbitrary system to collapse into a single clumpon. If the initial energy of the system is E_0, and initial mass is M, the energy of a single clumpon will be

$$E_f = M^2 G_0. \quad (17)$$

Then, the approximate time to collapse to a single clumpon from any initial conditions is given by combining (16) and (17):

$$t_* \simeq \frac{E_0 - E_f}{dE/dt[\rho = \text{clumpon}]} = \frac{E_0 - M^2 G_0}{M^3\mu\left(MH(0)\right)G_0^2} \quad (18)$$

In derivation of (18) we have assumed that dE/dt does not change much along the trajectories, so the initial conditions are close enough to a clumpon. Thus, this estimate for the time of collapse depends on only two integral quantities: initial energy and mass for initial conditions close to the final state.

4.3 Rate of blow up

The following analysis of the evolution of a density maximum reveals that the clumping process results from the nonlinear instability of the gradient flow in equation (6) when $D = 0$. For a particular case $G = G_0 e^{-|x|/\alpha}$ and $\mu(\overline{\rho}) = 1$, one may show that for a high enough peak, a density maximum $\rho_m(t) = \rho(x_m(t), t)$ becomes infinite in finite time. The motion of the maximum is governed by

$$\frac{d}{dt}\rho_m = \frac{1}{\alpha^2}\left(\rho_m^2 - \rho_m\Phi(x_m)\right) \geq \frac{1}{\alpha^2}\left(\rho_m^2 - \rho_m M\right), \quad (19)$$

where $M = \int \rho \mathrm{d}x$ is total mass and we have used the fact that Φ satisfies $\Phi - \alpha^2 \Phi_{xx} = \rho$. The last inequality holds, because $G \leq 1$ is bounded and ρ is everywhere positive. Thus, if at any point the maximum of ρ exceeds the (scaled) value of the total mass, then the value of the density maximum $\rho_m(t)$ must diverge in finite time. This divergence produces δ-functions in finite time. From (19), the density amplitude must diverge as $\rho_m \simeq \alpha^2/(t_0 - t)$. The formation of singularities in Fig. 2 occurs both at the maximum, and elsewhere. The subsidiary peaks eventually collapse with the main peak.

4.4 Dynamics of inflection points and collapse

Let us discuss in more detail the process by which density singularities are formed. Suppose the the initial condition contains only one density maximum. Then, one would expect the first singularity to form at the position of this maximum. As this density singularity forms, mass flows toward it. This causes a local reduction of density in the neighboring region from which the mass is flowing. Whenever this local reduction of density due to the formation of the singularity is sufficient to form a new maximum in density away from it, then the process of singularity formation starts again there, and so forth. In principle, this process could form an infinite number of density singularities. However, we propose two reasons why the expected number should be finite. First, the range of interaction is set by the length scale in H. Thus, one might expect no more clumpons to form than the ratio of the interaction range to the domain size. Second, in the formation of singularities from two nearby maxima, one of them may become stronger than the other and entrain it, thereby suppressing the formation of the second singularity. In practice, one sees the formation of considerably fewer clumpons than the number estimated by the ratio of the interaction range to the domain size. Hence, one may conjecture that the formation of singularities does involve some competition between neighboring density maxima. This conjecture could be tested by studying evolution from initial conditions containing several density maxima separated by varying distances which are comparable to, or smaller, than the average length scale in H.

A quantitative evaluation of this heuristic argument may be obtained by computing the position of the inflection point for the averaged density $\overline{\rho}$. Although no analytical formula for the motion of inflection point is available, one sees numerically that the inflection point quickly converges to the position of the singularity. The evolution of the inflection point corresponding to the

solution from Fig. 2 is shown in Fig. 3.

5 Formation of jammed states when mobility μ approaches zero

5.1 Competing length scales of H & G

An interesting limiting case arises when the scale of non-locality of H is much shorter than the range of the potential G. Formally, this limit corresponds to $H(x) \to \delta(x)$. In practice, we may select a sequence of piecewise smooth functions $H_\epsilon(x) = \exp(-|x|/\epsilon)/(2\epsilon)$ which converge weakly to a δ-function. For each function $H_\epsilon(x)$ in this sequence, no matter how small (but positive) the value of ϵ, the exact ODE reduction (13) still holds. So, what happens in the limit of very small epsilon, as $\epsilon \to 0$? In investigating this limit, we performed a sequence of numerical simulations for a fixed choice of the function $G(x) = \exp(-|x|/\alpha)$ while varying $H_\epsilon(x) = \exp(-x/\epsilon)/(2\epsilon)$ over a sequence of decreasing values of the ratio ϵ/α. This simulation is shown in Fig. 2 for $\epsilon/\alpha = 1/10$ and it demonstrates the formation of flat clumps of solutions. The mechanism for this phenomenon is the following. The vanishing mobility at $\overline{\rho} = 1$ caps the maximal density at $\overline{\rho} = 1$ in the long-term. This leads to the appearance of flat mesas in $\overline{\rho}(x)$ for large t. On the other hand, when $H(x) \to \delta(x)$, one finds $\overline{\rho}(x,t) \to \rho(x,t)$ pointwise in x, which forces $\rho(x,t)$ to develop a flat mesa, or plateau, structure in which the maximum is very close to unity, as well. This is precisely what is predicted for the chemotaxis equation with $H(x) = \delta(x)$ and $\mu(\rho) = 1 - \rho$ [24].

In the limit $H \to \delta$, model (6,7) recovers ordinary diffusion of local density. This is a singular limit, because it increases the order of the differentiation in the equation. Since ordinary diffusion is known to prevent collapse in one dimension [3], this singular limit should be of considerable interest for further analysis.

5.2 Stationary states

Numerical simulations of time-dependent problem (6,7) show that the solution converges to well-defined states with flat *mesa* peaks when $\mu(\overline{\rho})$ reaches 0 for some value of $\overline{\rho}$. In the remainder of this section, we shall concentrate on the analytical description of the evolution in this case. For simplicity of

formulas, we shall assume that the critical value of $\overline{\rho}$ is normalized to be 1, *i.e.*, $\mu(1) = 0$. In simulations, we shall take $\mu = 1 - \overline{\rho}$. However, all theoretical results, in particular, exact expressions for stationary sates, remain true for *arbitrary* dependence of $\mu(\overline{\rho})$, as long as $\mu(\overline{\rho})$ reaches 0 at some value of $\overline{\rho}$.

We distinguish two classes of stationary states, which differ mathematically and physically. Both classes of stationary states will describe a clump of particles whose density $\rho(x)$ is a generalized function with compact support, which we will call a *patch*. The difference between these classes lies in the physical reason for the vanishing of local velocity. Remember that local velocity is written as $\mathbf{u} = \mu(\overline{\rho})\nabla\Phi$. The solution is stationary if $\mathbf{u}$ vanishes at every point inside the patch. This can be achieved in two ways. First, $\nabla\Phi$ may be exactly zero everywhere inside the patch. In this case, the net force acting on every particle vanishes. These solutions are called *equilibrium* states. Second, it may also happen that the mobility μ vanishes at every point inside the patch. Physically, this corresponds to a clump at maximum density whose motion is prohibited, although the net force on each particle may not be zero. These solutions are called *jammed* states. Let us now study both the equilibrium and jammed states in more details. As we shall see, an analytical solution describing each of these states can be found. These solutions will also elucidate the nature of competing length scales in G and H. The stability of these solutions and their selection mechanisms will also also be demonstrated.

5.3 Equilibrium states

Let us assume for now that both the potential attraction $G(x)$ and the filter function $H(x)$ are proportional to the Green's function for the Helmholtz operator. This is both the case we use in numerical simulations, and also, incidentally, the only case we have found that admits analytical solution for stationary states. Thus, we posit

$$G(x) = \exp\left(-\frac{|x|}{\alpha}\right) \qquad\qquad H(x) = \frac{1}{2\beta}\exp\left(-\frac{|x|}{\beta}\right) \tag{20}$$

We are looking for stationary states $\rho(x)$ that are weak solutions with compact support, for which $\rho(x) = 0$ if $|x| > L$. While it is impossible to find a smooth (or even piecewise smooth) function $\rho(x)$ which is a stationary

solution of (6), one can find a stationary solution of the following form

$$\rho(x) = w\delta(x+L) + w\delta(x-L) + \begin{cases} 0, & |x| > L \\ \rho_0(x), & |x| \le L, \end{cases} \tag{21}$$

where the value of the constants w and L are to be determined.

For (21) to be a stationary (weak) solution, the following conditions must be satisfied:

$$\begin{aligned} \Phi(x) = (G * \rho)(x) = \text{const}, \quad & |x| < L \\ \overline{\rho}(x) = (H * \rho)(x) = 1, \quad & x = \pm L. \end{aligned} \tag{22}$$

Substitution of (21) into the first condition of (22) gives

$$\Phi(x) = wG(x-L) + wG(x+L) + \int_{-L}^{L} G(x-y)\rho_0(y)\mathrm{d}y = \text{const} \tag{23}$$

It is crucial to notice that if $G(x)$ is given by (20), then the integral in (23) must yield a function proportional to a sum of exponentials, which is only possible if $\rho_0(x)$ is a constant: $\rho_0(x) = \rho_0$. Performing the integral gives

$$\Phi(x) = we^{-|x-L|/\alpha} + we^{-|x+L|/\alpha} + \rho_0\alpha\left(2 - e^{-|x-L|/\alpha} - e^{-|x+L|/\alpha}\right) = \text{const} \tag{24}$$

which requires

$$w = \rho_0\alpha. \tag{25}$$

Enforcing the second condition in (22) will determine ρ_0 as a function of L. As in (23), we find an analytical expression for $\overline{\rho}$

$$\overline{\rho}(x) = \frac{w}{2\beta}\left(e^{-|x-L|/\beta} + e^{-|x+L|/\beta}\right) + \frac{\rho_0}{2}\left(2 - e^{-|x-L|/\beta} - e^{-|x+L|/\beta}\right) \tag{26}$$

Since (26) assumes identical values at $x = \pm L$, we need only check that $\overline{\rho}(x = L) = 1$. Substitution of $x = L$ into (26) gives

$$\rho_0\left[\alpha\left(1 + \exp\left(-2L/\beta\right)\right) + \beta\left(1 - \exp\left(-2L/\beta\right)\right)\right] = 2\beta \tag{27}$$

In principle, equation (27) already determines the density inside the patch as a function of length. It is, however, more practical to determine the length as a function of total mass of the clumpon M. The mass contained in the solution (21) is

$$M = \rho_0 L + 2w = \rho_0(L + 2\alpha).$$

Thus, we find an implicit condition for length L as a function of patch mass M:

$$M\left[\alpha\left(1+\exp\left(-2L/\beta\right)\right)+\beta\left(1-\exp\left(-2L/\beta\right)\right)\right]=2\beta(L+2\alpha) \qquad (28)$$

These solutions are shown on Fig. 5. It is interesting to note that (28) defines a non-negative length L only if the mass M is sufficiently large. This is perfectly physical: if the mass is small, there is no reason for the solution to "spread out", so a single δ-function is produced. Incidentally, this will happen if the mass of the clumpon $M = \int \rho \mathrm{d}x$ is such that $max_x\overline{\rho} < 1$, i.e., $M < 2\beta$. Physically, we expect that equilibrium solutions are unstable. Indeed, imagine a set of particles on a line positioned at an equal distance from each other. If the force between each pair of particles is repulsive, this configuration is stable, and the real part of all eigenvalues of the linearized problem is negative. However, if the force between the particles changes to purely attractive without changing the particle positions, this leads to the sign change of the eigenvalues which correspond to a stable situation. Thus, these equilibrium states with fixed gaps between the particles "held together" by purely attractive forces must be unstable, and must exhibit large values for the real parts of the unstable eigenvalues. Numerical analysis of linear stability of equilibrium states in the continuum description confirms this intuitive physical picture. Namely, there exists a set of eigenvalues with large positive real parts. In addition, a fully nonlinear time-dependent simulation of (6,7) starting with initial conditions corresponding to even slightly perturbed equilibrium states shows very rapid deviation away from equilibrium. Therefore, equilibrium states are *unstable* and will never be realized in nature.

5.4 Jammed states

The derivation of the jammed states is rather similar to that for the equilibrium states, so only a brief discussion of it will be provided. Let us again assume that stationary states $\rho(x)$ are weak solutions with compact support, and $\rho(x) = 0$ if $|x| > L$:

$$\rho(x) = w\delta(x+L) + w\delta(x-L) + \begin{cases} 0, & |x| > L \\ \rho_0(x), & |x| \le L \end{cases} \qquad (29)$$

Now, for solution (29) to be a jammed solution, we need just one condition:

$$\overline{\rho}(x) = (H * \rho)(x) = 1, \qquad |x| \le \pm L. \qquad (30)$$

Substituting (29) into condition (30) gives

$$\overline{\rho}(x) = wH(x-L) + wH(x+L) + \int_{-L}^{L} H(x-y)\rho_0(y)\mathrm{d}y = 1 \qquad (31)$$

Again, it is essential that $H(x)$ is given by (20), so the integral in (23) must be proportional to a sum of exponentials, which is only possible if $\rho_0(x)$ is a constant: $\rho_0(x) = \rho_0$. Equation (31) transforms to

$$\overline{\rho}(x) = \frac{w}{2\beta}\left(e^{-|x-L|/\beta} + e^{-|x+L|/\beta}\right) + \frac{\rho_0}{2}\left(2 - e^{-|x-L|/\beta} - e^{-|x+L|/\beta}\right) = 1 \quad (32)$$

which requires

$$w = \beta \qquad\qquad \rho_0 = 1 \qquad (33)$$

The mass contained in the solution (21) is

$$M = \rho_0 L + 2w = L + 2\beta.$$

The jammed states are illustrated on Fig. 6.

To understand the nonlinear stability of jammed states, let us again appeal to the physical picture of particles on a line. *Jammed* states correspond to a set of finite-size particles pressed tightly together. Physical intuition tells us that such a state should be favorable for purely attractive forces between pairs of particles. Numerical analysis of linear stability of *jammed* states in the continuum approximation confirms this: the real part of the spectrum is isolated from 0 by $-D$, where $\lambda = -D$ is the limiting point of spectral sequence. Thus, D should determine the time scale for convergence to stationary solutions. That is, the rate of convergence to stationary solution is given by the time scale $\tau \sim 1/D$.

To verify these predictions, a fully nonlinear simulation starting with a smooth initial conditions in the form of Gaussian peak has been performed. The results of this simulation are given in Fig. 7. For $D = 0.01$ used in the simulation, the solution becomes practically stationary after $t \sim 100$. The small "bumps" at the position of the δ-functions in density correspond to a mismatch in the stationary solutions, which were derived for $D = 0$. The amplitudes of the "bumps" tend to zero when D becomes very small.

6 Jammed stationary states in two dimensions

6.1 Exact jammed states in two dimensions

While this paper focuses primarily on the evolution of particles in one dimension, the real-world technological importance of self-assembly processes requires us to derive and analyze stationary solutions of our model in two dimensions. Numerical simulations of particle dynamics [27] show that there is a tendency for the formation of isolated clumps of either roughly circular shape, or, for high particle densities, roughly circular or elliptical voids in fully dense areas. To model these results, let us assume that the mobility $\mu(\overline{\rho})$ vanishes at critical density $\overline{\rho} = 1$, and ρ and $\overline{\rho}$ are connected through the two-dimensional Helmholtz operator

$$\overline{\rho} - \beta^2 \Delta \overline{\rho} = \rho\,, \quad \text{so that} \quad \overline{\rho} = H * \rho\,. \tag{34}$$

Inspired by these results we use the intuition developed in one dimension to seek jammed solutions in two dimensions which are fully dense $\overline{\rho} = 1$ inside an area D with additional distributed δ-function for density on the boundary ∂D, and $\rho = 0$ in the exterior of D. Remarkably, when H is the Green's function for the Helmholtz operator, an exact analytical expression for several possible shapes of D can be found. Again, we shall emphasize that our results will hold for an *arbitrary* functional dependence $\mu(\overline{\rho})$ as long as the mobility vanishes for some value of $\overline{\rho} = \overline{\rho}_*$. For convenience, we have again rescaled the critical value to be $\overline{\rho}_* = 1$.

Consider an orthogonal coordinate system (ξ, η) for which the solution of Helmholtz equation separates variables. Suppose, in addition, that the boundary of D corresponds to one of the coordinate lines $\xi = \xi_0$, and interior of D is given by $\xi < \xi_0$ Then, we may seek the solution in the exterior of D in the form $\overline{\rho}(\xi, \eta) = F(\xi/\beta)G(\eta/\beta)$. Boundary conditions for the exterior of D are $\overline{\rho} \to 0$ as $\xi \to +\infty$, and boundary conditions at $\xi = \xi_0$ are obtained by continuity of $\overline{\rho}$ at the boundary. Since for jammed states $\overline{\rho} = 1$ in the interior, the continuity condition gives $\overline{\rho} = 1$ on the boundary. Therefore, separable solutions must take the form $\overline{\rho}(\xi, \eta) = F(\xi/\beta)/F(\xi_0/\beta)$. Since the system of coordinates is orthogonal and $\rho = 1$ in the interior of D from (34), we can compute the amplitude of δ-function for density ρ at the boundary $\xi = \xi_0$, which comes out to be $-\beta F'(\xi_0/\beta)/F(\xi_0/\beta)$. Thus, the exact solution

for the case when separation of variables of Helmholtz equation is possible and the boundary is given by $\partial D = \{\xi = \xi_0\}$ is

$$\rho(\xi,\eta) = \begin{cases} 1, & (\xi,\eta) \in \mathrm{int}D \\ -\delta(\xi-\xi_0)\beta F'(\xi_0/\beta)/F(\xi_0/\beta) & (\xi,\eta) \in \partial D \\ 0, & (\xi,\eta) \in \mathrm{ext}D \end{cases} \tag{35}$$

$$\overline{\rho}(\xi,\eta) = \begin{cases} 1, & (\xi,\eta) \in \mathrm{int}D \\ F(\xi/\beta)/F(\xi_0/\beta), & (\xi,\eta) \in \mathrm{ext}D \end{cases} \tag{36}$$

To be specific, in Table 1 we enumerate all cases for which separation of variables in Laplace/Helmholtz equation is possible. As it is known, Helmholtz equation in two dimensions is separable in four coordinates only: Cartesian (which we shall not consider here), cylindrical, elliptic cylindrical and parabolic cylindrical [28]. Each of these cases selects a particular shape of the patch, as well as a particular form of the function $F(\xi)$.

Coordinates	*Shape of D*	*Functional form of* $F(\xi)$
Cylindrical	Circle	Bessel function $K_0(r)$
Elliptic cylindrical	Ellipse	Modified Matthew Function
Elliptic cylindrical	Hyperbolae	Matthew Function
Parabolic cylindrical	Parabola	Parabolic Cylinder Function

Table 1: A summary of exact jammed solutions and corresponding shapes in two dimensions

Of course, similar results may be obtained in three dimensions, where eleven coordinate systems exist for which the Helmholtz differential equation is separable. We shall not go into details here as, first of all, the generalization is straightforward, and, second, we are only interested here in one- and two-dimensional self-assembly. Three-dimensional analogues of self-assembly may be important for some models arising in mathematical biology which are discussed at the end of Sec.7.

6.2 Irregular shapes: asymptotic result

For arbitrary shape of domain D, it is no longer possible to find an exact expression for densities ρ and $\overline{\rho}$. However, we may find an *asymptotic* result which shows that δ-function density on the boundary must be a slowly-varying function of the boundary coordinates in the case when β – the range

of H – is small compared to the size of the patch. We consider a patch of an arbitrary simple-connected shape Ω with a smooth boundary and introduce the coordinate η along the boundary of the patch $\partial\Omega$. Considerations of one dimensional case indicate that the patch is stable if it is jammed, i.e. $\mu = 0$ everywhere inside the patch, which leads to equation $\overline{\rho} = 1$ inside the patch. For now, we consider $H(x)$ to be inverse Hemholtz operator, thus $\overline{\rho}$ satisfies (34). Thus, inside the patch, we necessarily have $\rho = 1$. The decay of $\overline{\rho}$ close to the boundary should be compensated by the presence of delta-function concentration at the boundary. Let us assume that the boundary is smooth. If ξ is the coordinate locally perpendicular to the boundary and the boundary is at $\xi = \xi_0$, then we assume that the density near the boundary has the form:

$$\rho(\xi \sim \xi_0) = f(\eta)\delta(\xi - \xi_0) + \mathrm{ind}_\Omega(\mathbf{r}), \tag{37}$$

where $\mathrm{ind}_\Omega(\mathbf{r})$ is the indicator function which equals unity. if $\mathbf{r} \in \Omega$ and vanishes otherwise. From the condition $\overline{\rho} = 1$ and $\rho = 1$ in the interior of Ω we obtain an integral equation for the strength $f(s)$:

$$\int_{\partial\Omega} f(s)H(\mathbf{r} - \mathbf{r}(s'))\mathrm{d}s' + \int_\Omega H(\mathbf{r} - \mathbf{r}')\mathrm{d}\mathbf{r}' = 1 \tag{38}$$

If $\mathbf{r}$ is farther than β away from the boundary, then only the contribution from the second integral is relevant. However, due to the extremely short range of H, this integral is equal to unity and equation (38) gives an identity. Thus, we only need to investigate equation (38) in the case when the distance between $\mathbf{r}$ and the boundary is of order β or less. Suppose this distance is $d\beta$ with $d > 0$ being a constant of order unity or less. Since $H(\mathbf{r}' - \mathbf{r})$ decays rapidly away from $\mathbf{r}$ for distances larger than β, we can approximate the slowly varying function $f(s')$ by its value at s, and the integral (38) as

$$f(s)\int_{\partial\Omega} H(\mathbf{r} - \mathbf{r}(s'))\mathrm{d}s' + \int_\Omega H(\mathbf{r} - \mathbf{r}')\mathrm{d}\mathbf{r}' = 1 \tag{39}$$

Since we are only interested in the immediate neighborhood of the point $\mathbf{r}(\eta)$, we will now assume that the boundary is locally straight and vertical, and the interior of the patch is to the right of the boundary. We introduce the local coordinates $x = \beta\xi$ and $y = \beta\eta$ centered at the point $\mathbf{r}$, so the boundary is at $x = d$ and the $x-$axis is pointing towards the boundary. Note the exact form of the kernel H

$$H(\mathbf{r}) = \frac{1}{2\pi\beta^2} K_0\left(\frac{|\mathbf{r}|}{\beta}\right). \tag{40}$$

We split up the second integral in (39) and perform the integration exactly by going to polar coordinates (and skipping algebraic details):

$$\int_\Omega H(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}' \simeq \frac{1}{2\pi}\int_{x<d} K_0\left(\sqrt{x^2+y^2}\right)\mathrm{d}x\mathrm{d}y = \tag{41}$$

$$= 1 - \frac{1}{2\pi}\int_{x>d} K_0\left(\sqrt{x^2+y^2}\right)\mathrm{d}x\mathrm{d}y = 1 - \frac{1}{2}e^{-d}$$

Let us now compute the first integral in (39). We have:

$$\int H(\mathbf{r}(s)-\mathbf{r}(s'))\mathrm{d}s' = \frac{1}{2\pi\beta}\int_{y=-\infty}^{+\infty} K_0\left(\sqrt{d^2+y^2}\right)\mathrm{d}y = \frac{1}{2\beta}e^{-d}$$

Thus, equation (39) becomes

$$f(\eta)\frac{1}{2\beta}e^{-|\mathbf{r}-\mathbf{r}'|/\beta} + 1 - \frac{1}{2}e^{-|\mathbf{r}-\mathbf{r}'|/\beta} = 1 \tag{42}$$

so the answer is simply

$$f(\eta) = \beta. \tag{43}$$

Thus, for a smooth boundary, jammed states are obtained by the same principle as in one dimension: the densely packed state $\rho = \overline{\rho} = 1$ inside the domain is surrounded by a δ-function layer of strength β. At first glance, the asymptotic answer (43) seems not correspond to the exact answer (35) for circular, elliptic and parabolic shapes. Consider, however, the case of a circular patch as an example. Assume that the boundary of the patch being at $r = r_0$. According to (35), the strength of δ-function on the boundary is

$$f = -\beta\frac{K_0'\left(r_0/\beta\right)}{K_0\left(r_0/\beta\right)} = \beta\frac{K_1\left(r_0/\beta\right)}{K_0\left(r_0/\beta\right)}$$

The ratio of Bessel functions converges rapidly to 1 for $\beta \to 0$. In fact, this ratio is extremely close to 1 already when $\beta < r_0$. Since β is assumed small, for a patch of any reasonable size (larger than several units of β), the approximate result (43) is valid to high accuracy (exponential in β). In general, we can only postulate that the accuracy of (43) should be $O(\beta^2)$, since we neglected the local curvature of the surface. Introduction of local curvature effects will change the asymptotic result (43), but this correction is bound to be small (of the order β^2) when $\beta \to 0$.

6.3 Numerical simulation of states in two dimensions

To illustrate these exact and asymptotic results, we have performed fully nonlinear numerical simulations for $\alpha = 1$, $\beta = 0.1$ and $D = 0.01$ in two dimensions. The results of this simulations are shown in Fig. 8. gaussian radial distribution. Evolution due to (6,7) deforms this shape into a flat-top elliptical shape, which is reminiscent of the solutions derived in Sec.6.1. We conjecture that elliptical shapes are more stable than circular shapes, although a detailed analysis of the two-dimensional stability and selection mechanism has yet to be completed.

7 Conclusion, open problems and further applications

A new model was proposed and analyzed for the collective aggregation of finite-size particles driven by the force of mutual attraction. Starting from smooth initial conditons, the solution for the particle density in this model was found to collapse into a set of delta-functions (clumps), and the evolution equations for the dynamics of these clumps were computed analytically. The energy derived for this model is well defined even when density is supported on δ-functions. The mechanism for the formation of these δ-function clumps is the nonlinear instability governed by the Ricatti equation (19), which causes the magnitude of any density maximum to grow without bound in finite time. At first sight, it may seem that the emergence of δ-function peaks in the solution might be undesirable and perhaps should be avoided. However, these δ-functions may be understood as clumps of matter, and the model guarantees that any solution eventually ends up as a set of these clumps. Subsequently, further collective motion of these clumps may be predicted using a (rather small-dimensional) system of ODEs, rather than dealing with the full non-local PDEs. The question of how many clumps arise from a given initial condition remains to be considered. One may conjecture that clump formation is extensive; so that each clump forms from the material within the range of the potential Φ, determined by G. On a longer time scale, the clumps themselves continue to aggregate, as determined by the collective dynamics (13) of weak solutions (12). This clump dynamics is also a gradient flow; so that eventually only one clump remains.

A comparison with point vortex solutions of Euler's equations for ideal

hydrodynamics in two-dimensions may be made here. Prediction of the incompressible motion of an ideal fluid is governed by a set of nonlinear PDE in which pressure introduces non-locality. A drastic simplification of motion occurs, when all the vorticity is concentrated in delta-functions (point vortices) [30]. The motion of point vortices lies on a singular invariant manifold: if started with a set of point vortices, the fluid structure will remain a set of point vortices. However, a smooth initial condition for vorticity *does not* split into point vortices under the Euler motion. In the present model, though, the physical attraction drives any initial distribution of density towards a set of delta-functions, so one is *guaranteed* to obtain effectively finite-dimensional behavior in the system after a rather short initial time. Of course, this time depends of the precise form of the long range attraction.

Because two scales are present in the smoothing functions H and G, the effects of boundary conditions warrant further study. For example, the $H \to \delta$ limit should also allow formation of boundary layers. These boundary issues were avoided in the present treatment by using periodic boundary conditions. However, it would be natural in some physical situations to apply, e.g., Neumann boundary conditions to the particle flux $\mathbf{J}$. The issue of boundary conditions will arise and must be addressed on an individual basis in specific applications of these equations in physics, chemistry, technology and biosciences.

Our approach involving a variational principle, energy and competition of length scales is relevant for many areas of science. In particular, we have recently learned that our variational approach is applicable to bio-sciences, in particular, to the theory of insect swarming. In a recent work, Topaz *et al.* [31] have discovered the formation of isolated patches of matter (*swarms*) in a variant of (6,7) with a *nonlinear* instead of *nonlocal* diffusion. The variational energy (8) for their model was

$$E[\rho] = \int \rho G * \rho - \frac{D}{2}\rho^2$$

This case could be considered as an extension of our model for $H(x) = \delta(x)$, $\mu(\overline{\rho}) = 1$ and

$$E[\rho] = \int \rho G * \rho - DQ(\overline{\rho})$$

with $Q'(\overline{\rho}) \geq 0$, in particular, $Q(\overline{\rho}) = \overline{\rho}^2/2$. Alternatively, a variant of this nonlinear diffusion model can be derived if we start with $\mu(\overline{\rho}) = 1 - \overline{\rho}$ and

$D = 0$. We can then rewrite (6) as

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \nabla \Phi) = \operatorname{div}(\rho \overline{\rho} \nabla \Phi),$$

which, again, is a modification of swarming models considered in [31] with non-local diffusion. We emphasize that, in our opinion, nonlocality in diffusion is advantageous, since it allows for simple generalized solutions in terms of constants and δ-functions. These generalized solutions dominate both the dynamics and statics of the problem and greatly simplify the analytical treatment.

Acknowledgments. We thank S. R. J. Brueck, P. Constantin, B. J. Geurts, J. Krug and E. S. Titi for encouraging discussions and correspondence about this work. DDH is grateful for partial support by US DOE, under contract W-7405-ENG-36 for Los Alamos National Laboratory, and Office of Science ASCAR/AMS/MICS. VP was partially supported by funding from US DOE, DE-FG02-04ER-46119 and Petroleum Research Grant 40218-AC9.

References

[1] Debye, P., and E. Hückel. 1923. Zur Theorie der Elektrolyte: (2): Das Grenzgesetz für die Elektrische Leiftfahrigkeit (*On the theory of electrolytes 2: limiting law of electircal conductivity*). *Phys. Z.* 24:305-325 (1923).

[2] E. F. Keller and L. A. Segel, *J. Theo. Biol.* 26 (1970) 399-415; *Ibid. J. Theo. Biol.*, 30 (1971) 225-234.

[3] D. Horstmann, *MPI Leipzig Report* (2003).

[4] S. Chandrasekhar, *An introduction to the theory of stellar structure* (Dover, 1939).

[5] Barcilon, V., D. P. Chen, and R. S. Eisenberg. 1992. Ion flow through narrow membrane channels. II. *SIAM J. Appl. Math.* 52:1405-1425.

[6] Syganow, A. N., and E. von Kitzing. 1995. The integral weak diffusion and diffusion approximations applied to ion transport through biological ion channels. J. Phys. Chem. 99:12030-12040.

[7] Syganow, A. N., and E. von Kitzing, (In)validity of the Constant Field and Constant Currents Assumptions in Theories of Ion Transport. *Biophysical Journal*, Volume 76 February 1999 768-781.

[8] Selberherr, S. 1984. *Analysis and Simulation of Semiconductor Devices.* Springer-Verlag, Wien.

[9] J. Villain, *J. Phys. France I* **1**, 19 (1991).

[10] D. Xia and S. R. J. Brueck *A Facile Approach to Directed Assembly of Patterns of Nanoparticles Using Interference Lithography and Spin Coating*, *Nano Letters*, **4**, 1295-1299 (2004).

[11] K. Mertens, V. Putkaradze, D. Xia and S. Brueck, *J. Appl. Phys.*, under consideration (2005).

[12] J.E.G.J Wijnhoven, and W.L Vos, *Science* **281**, 802 (1998).

[13] B. Gates, and Y. Xia, *Appl. Phys. Lett.* **78**, 3178 (2001).

[14] C.A. Ross, S. Haratani, F.J. Castano, Y. Hao, M. Hwang, M. Shima, J.Y. Cheng, B. Vogeli, M. Farthoud, M. Walsh, and H.I. Smith, *J. Appl. Phys.* **91**, 6848 (2002).

[15] R. Moller, A. Csaki, J.M. Kohler, and W. Fritzsche, *Langmuir* **17**, 5426 (2001).

[16] F.J. Castan, Y. Hao, M. Hwang, C.A. Ross, B. Vogeli, H.I Smith, and S. Haratani, *Appl. Phys. Lett.* **79**, 1504 (2001).

[17] W. Fritzsche, A. Csaki, and R. Moller, *Proceedings of the SPIE*, **4626**, 17 (2002).

[18] A. von Blaaderen, R. Ruel, and P. Wiltzius, *Nature* **385**, 321 (1997).

[19] S.M. Yang, and G.A. Ozin, *Chem. Comm.* 2507 (2000).

[20] H. Zheng, I. Lee, M.F. Rubner, and P.T, Hammond *Adv. Mater.* **14**, 569 (2002).

[21] A. M. Leshanski and M. Y. Rubinstein, *Phys. Rev. E*, **71** 040601(R) (2005).

[22] P. A. Kralchevsky, K. Nagayama *Adv. Coll. Int. Sci.* **85**, 145 (2000).

[23] D. Vella and L. Mahadevan, arXiv:cond-mat/0411688 (2005).

[24] J. J. L. Velazquez, *SIAM J. Appl. Math*, **64**, 1664 (2004).

[25] D. D. Holm, J. E. Marsden and T. S. Ratiu, *Adv. in Math.*, **137** (1998) 1-81. http://xxx.lanl.gov/abs/chao-dyn/9801015.

[26] F. Otto, *Comm. Partial Differential Equations*, 26(1-2):101-174 (2001).

[27] S. Maenosono, C.D. Dushkin and Y.Yamaguchi, *Colloid Polym. Science* **277**, 993 (1999).

[28] P. Morse, H. Feshbach, *Methods of Theoretical Physics* , McGraw-Hill (1953).

[29] J. Marsden, T. Ratiu, *Introduction to Mechanics and Symmetry*, 2nd ed., Springer (2002).

[30] Saffman, P. G. *Vortex Dynamics*. Cambridge University Press (1992).

[31] C. M. Topaz, A. L. Bertozzi and M. A. Lewis, ArXiv: q-bio PE/0504001 (2005).

Figure Captions

Figure1. Scanning Electron Microscope (SEM) figures of self-assembly of particles in nano-channels, courtesy of S. R. J. Brueck and D. Xia. Note fully dense clumps separated by voids, evident in cases B, C and F. Cross-width of the channels as well as distance between the channels is 100 nm.

Figure2. Numerical simulation demonstrates the emergence of particle clumps, showing formation of density peaks in a simulation of the initial value problem for equation (6) using smooth initial conditions for density with $l = 1$, $G(x) = H(x) = \exp(-|x|)$, $\mu(\overline{\rho}) = 1$. The vertical coordinate represents $\overline{\rho} = H * \rho$, which remains finite even when the density forms δ-functions.

Figure 3. Position of inflection point for simulation shown on Fig. 2. The dashed line in the bottom shows the minimum value allowed by the finite resolution of the mesh. In this case particular case, this minimum value is equal 0.1 with the length of the interval being 10.

Figure 4. Evolution of a Gaussian initial condition for ρ(x,0) with $\mu(\overline{\rho}) = 1 - \overline{\rho}$ and $H = \exp(-|x|/\epsilon)/(2\epsilon)$ where $\epsilon = \alpha/10$. The solution quickly forms a plateau of maximal possible density ($\rho_{\max} = 1$).

Figure 5. Stationary equilibrium solution for $\alpha = 1$, $\beta = 0.1$ and $L = 1$. Top $\rho(x)$ (with representation of δ-functions at $x = \pm L$ as vertical red lines). Middle: $\Phi = (G * \rho)(x)$ for the same solution. Bottom: $\overline{\rho} = H * \rho$ for the same solution.

Figure 6. Stationary jammed states for $\alpha = 1$, $\beta = 0.1$ and $L = 1$. Top $\rho(x)$ (again, δ-functions at $x = \pm L$ are represented by vertical red lines). Middle: the potential $\Phi = (G * \rho)(x)$. Bottom: $\overline{\rho} = H * \rho$.

Figure 7. Convergence to analytic equilibrium solution (circles) for different times (colored solid lines, see legend). In simulation, $D = 0.01$, $\alpha = 1$, $\beta = 0.1$

Figure 8. Two-dimensional evolution of a gaussian initial profile for consecutive times with $D = 0.01$, $\alpha = 1$, $\beta = 0.1$

This figure "Figure1.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1

This figure "Figure2.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1

This figure "Figure3.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1

This figure "Figure4.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1

This figure "Figure5.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1

This figure "Figure6.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1

This figure "Figure7.jpg" is available in "jpg" format from:

http://arXiv.org/ps/nlin/0506020v1


This figure "Figure8.jpg" is available in "jpg" format from:
http://arXiv.org/ps/nlin/0506020v1